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### **X-ray Absorption Studies for Poly(vinylferrocene) Polymers for Anion Separation**

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**Introduction:** Many industrial contaminants exist as anions. These include high-priority pollutants such as chromate, pertechnetate, and nitrate ions. Technetium is an important and difficult pollutant in nuclear waste. Because of its half-life of 213,000 years, technetium ( $^{99}\text{Tc}$ ) presents a long-term hazard for waste disposal. Much of the  $^{99}\text{Tc}$  in the tank wastes is present as pertechnetate ( $\text{TcO}_4^-$ ), accounting for its high solubility and mobility in aqueous systems. Conventional sorbents such as commercial ion exchange resins can be used to extract  $\text{TcO}_4^-$ . However chemical elution of the ion exchange resin generates unwanted secondary wastes. An attractive alternative is to use an electrically conducting polymer [e.g. polyvinyl ferrocene] (PVFc) to separate technetium from nitrate in high-level liquid nuclear waste. Absorption and elution can be done electrochemically without the generation of secondary wastes. The work reported here involves the use of in situ x-ray absorption spectroscopy (XAS) to study the interaction of anions with conductive polymer poly(vinylferrocene) electrodes. Perrhenate salts were used as non-radioactive surrogates for pertechnetate.

**Methods and Materials:** Several types of PVFc electrodes were investigated. The electrodes were prepared by electrodeposition on a carbon cloth substrate from 2mM PVFc with tetrabutylammonium perrhenate ( $\text{TBAREO}_4$ ) in a  $\text{CH}_2\text{Cl}_2$  solvent. Alternatively, electrodes with higher PVFc loading was achieved by dip coating carbon cloth in 2mM PVFc solutions in a  $\text{CH}_2\text{Cl}_2$  solvent. Electrodes based on modified PVFc materials, developed at PNNL, were also prepared using the dip coating technique. A special spectro-electrochemical cell was designed and built for in situ XAS studies at both the Fe K edge and the Re  $L_3$  edge. Electrochemical studies and in situ XAS were done in a cell with 0.1 M  $\text{NH}_4\text{ReO}_4$  solution. XAS spectra were also obtained on several standard compounds such as various iron oxides, ferrocene, ferrocenium hexafluorophosphate, ferrocenium tetrafluoroborate, ferrocenium perrhenate and dimethyl ferrocenium perrhenate.

**Results:** In situ methods have been developed for obtaining high-quality XAS spectra for electroactive polymers based on PVFc and modified PVFc. The XAS results indicate that >80% of the ferrocene moieties in the polymers are oxidized at positive potentials. Oxidation of ferrocene to ferrocenium yields the expected edge shift in the Fe K edge XANES. The Fe-C bonds are longer in the ferrocenium compounds. There is no solid direct evidence from the Fe XAS showing interaction of Fe with the  $\text{ReO}_4^-$  anion in ferrocenium perrhenate or in the oxidized polymer. This may be due to the highly delocalized charge on the ferrocenium. A slight decrease in the intensity of the Re- $L_3$  white line of  $\text{ReO}_4^-$  in the oxidized polymer may be indicative of a slight distortion of the  $\text{ReO}_4^-$  tetrahedron due to interaction with the ferrocenium.

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